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出願人
Applicant (s): 住友特殊金属株式会社

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特許庁長官
Commissioner,
Patent Office

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Date of Application: May 14, 1999

Application Number: Patent Application No. 11-134998

Applicant(s): Sumitomo Special Metals Co., Ltd.

May 12, 2000

Commissioner,
Patent Office Takahiko Kondo

Certificate No. 2000-3034440

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[NAME OF DOCUMENT] PATENT APPLICATION
[REFERENCE NUMBER] 99P030SM
[TO] Commissioner, Patent Office
[INTERNATIONAL CLASSIFICATION] C23C 14/00
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[INDICATION OF FEE]
[NUMBER OF PREPAYMENT ACCOUNT] 070140
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[NAME OF DOCUMENT] Specification 1
[NAME OF DOCUMENT] Drawings 1
[NAME OF DOCUMENT] Abstract 1
[PROOF] Required

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[NAME OF DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION] SURFACE TREATING PROCESS AND SURFACE TREATING APPARATUS

[SCOPE OF CLAIMS OF PATENT]

[CLAIM 1] A surface treating process for forming a vapor deposited film from an easily oxidizable vapor-depositing material on the surface of a work, comprising the step of producing a desired vapor deposition controlling gas atmosphere in zones near a vapor-depositing material and the work by evaporating a wire-shaped vapor-depositing material containing a vapor deposition controlling gas, while supplying such material to the melting/evaporating source of the vapor-depositing material.

[CLAIM 2] A surface treating process according to claim 1, wherein said vapor deposition controlling gas is hydrogen gas.

[CLAIM 3] A surface treating process according to claim 2, wherein the molar ratio of hydrogen to oxygen in at least a space between the vapor-depositing material and the work within the vacuum treating chamber is in a range of 10 to 250.

[CLAIM 4] A surface treating process according to claim 3, wherein the molar ratio of hydrogen to oxygen in at least a space between the vapor-depositing material and the work within the vacuum treating chamber is in a range of 20 to 150.

[CLAIM 5] A surface treating process according to claim 2, wherein said vapor-depositing material is evaporated resulting in a hydrogen concentration in said vapor deposited film in a

range of 1 to 20 ppm.

[CLAIM 6] A surface treating process according to claim 5, wherein said vapor-depositing material is evaporated resulting in a hydrogen concentration in said vapor deposited film in a range of 2 to 15 ppm.

[CLAIM 7] A surface treating process according to claim 2, wherein said wire-shaped vapor-depositing material is an aluminum wire having a content of hydrogen in a range of 0.5 to 11 ppm.

[CLAIM 8] A surface treating process according to claim 7, wherein said wire-shaped vapor-depositing material is an aluminum wire having a content of hydrogen in a range of 2 to 5 ppm.

[CLAIM 9] A surface treating process according to any of claims 1 to 8, wherein the evaporation of said vapor-depositing material is carried out under a partial pressure of oxygen equal to or higher than 10^{-3} Pa.

[CLAIM 10] A surface treating process according to any of claims 1 to 9, wherein said work is a rare earth metal-based permanent magnet.

[CLAIM 11] A surface treating apparatus comprising a vacuum treating chamber connected to a evacuating system, a melting/evaporating source for melting and evaporating a wire-shaped vapor-depositing material containing a vapor deposition controlling gas, a member for retaining a work on which the vapor-depositing material is deposited, said

melting/evaporating source and said work retaining member being disposed in the vacuum treating chamber, and a vapor-depositing material supply means for supplying said wire-shaped vapor-depositing material containing the vapor deposition controlling gas to said melting/evaporating source.

[CLAIM 12] A surface treating apparatus according to claim 11, wherein said vapor-depositing material supply means comprises a feed reel for feeding said wire-shaped vapor-depositing material.

[CLAIM 13] A surface treating apparatus according to claim 11 or 12, wherein said vapor deposition controlling gas is hydrogen gas.

[CLAIM 14] A surface treating apparatus according to any of claims 11 to 13, wherein the molar ratio of said vapor deposition controlling gas to oxygen can be adjusted by the feed rate of said vapor-depositing material fed from said feed reel.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[TECHNICAL FIELD TO WHICH THE INVENTION BELONGS]

The present invention relates to a surface treating process for vapor-depositing an easily oxidizable material such as aluminum and zinc onto a work such as a rare earth metal-based permanent magnet, and a surface treating apparatus suitable for carrying out such process.

[0002]

[PRIOR ART]

For a rare earth metal-based permanent magnet having a nature that it is liable to be deteriorated by oxidation, for example, it is a conventional practice to form an aluminum film on the surface of the magnet by vapor deposition to prevent the deterioration of the magnet caused by oxidation. A surface treating apparatus, for example, as shown in Fig.3, is employed for such a treating process.

Fig.3 shows an apparatus for forming a vapor deposited film of aluminum on a magnet, more specifically, a rare earth metal-based permanent magnet. A plurality of hearths 2, each of which is a melting/evaporating source for evaporating aluminum 10 as a vapor-depositing material, are disposed on a hearth support base 4 risen on a support table 3 in a lower portion of a vacuum treating chamber 1 connected to an evacuating system which is not shown. Two cage-shaped work retaining members 5 each formed of a net-shaped material are disposed side-by-side for rotation about rotary shafts 6 in an upper portion of the vacuum treating chamber 1.

This apparatus is designed, so that rare earth metal-based magnets 30 as works are placed into each of the work retaining members 5, and the aluminum 10 is evaporated from the hearth 2 heated to a predetermined temperature by a heating means (not shown), while rotating the work retaining members 5, thereby forming a vapor deposited film of aluminum on the surface of each of the rare earth metal-based permanent magnets30 in the work retaining members 5.

[0003]

[PROBLEM TO BE SOLVED BY THE INVENTION]

However, when the vapor deposition process is carried out using such vapor deposition apparatus in an atmosphere particularly under a high partial pressure of oxygen in the vacuum treating chamber, the aluminum evaporated from the melting/evaporating source, before reaching the works, is oxidized and as a result, an aluminum film having an excellent quality cannot be formed. In addition, the apparatus suffers from a problem that an aluminum oxide film is formed on the molten aluminum within the melting/evaporating source and for this reason, aluminum as the evaporating material is sufficiently not evaporated. If an attempt is made to increase the degree of vacuum for reducing the partial pressure of oxygen, it is necessary to carry out an evacuation for a long time. Therefore, if the time taken for the overall processing is supposed to be, for example, 2.5 hours, one hour is required for providing a degree of vacuum equal to or lower than 10^{-4} Pa, resulting in a problem of a poor productivity.

[0004]

[MEANS FOR SOLUTION OF PROBLEM]

Accordingly, as a result of zealous studies made to solve the above problems, the present inventors have found that by evaporating a wire-shaped vapor-depositing material containing a vapor deposition controlling gas such as hydrogen gas, while supplying such material to the melting/evaporating source of

the vapor-depositing material, it is possible to evaporate the vapor-depositing material in a state in which a desired gas atmosphere has been produced in at least zones near the vapor-depositing material and the work within the vacuum treating chamber, thereby making it possible to solve the problems which existed in a conventional process as described above, without use of a special apparatus for providing a high degree of vacuum.

[0005]

A surface treating process according to the present invention has been accomplished based on the above knowledge in view, and to achieve the above object, according to claim 1, there is provided a surface treating process for forming a vapor deposited film from an easily oxidizable vapor-depositing material on the surface of a work, comprising the step of producing a desired vapor deposition controlling gas atmosphere in zones near a vapor-depositing material and the work by evaporating a wire-shaped vapor-depositing material containing a vapor deposition controlling gas, while supplying such material to the melting/evaporating source of the vapor-depositing material.

According to claim 2, in addition to claim 1, the vapor deposition controlling gas is hydrogen gas.

According to claim 3, in addition to claim 2, the molar ratio of hydrogen to oxygen in at least a space between the vapor-depositing material and the work within the vacuum treating chamber is in a range of 10 to 250.

According to claim 4, in addition to claim 3, the molar ratio of hydrogen to oxygen in at least a space between the vapor-depositing material and the work within the vacuum treating chamber is in a range of 20 to 150.

According to claim 5, in addition to claim 2, the vapor-depositing material is evaporated resulting in a hydrogen concentration in the vapor deposited film in a range of 1 to 20 ppm.

According to claim 6, in addition to claim 5, the vapor-depositing material is evaporated resulting in a hydrogen concentration in the vapor deposited film in a range of 2 to 15 ppm.

According to claim 7, in addition to claim 2, the wire-shaped vapor-depositing material is an aluminum wire having a content of hydrogen in a range of 0.5 to 11 ppm.

According to claim 8, in addition to claim 7, the wire-shaped vapor-depositing material is an aluminum wire having a content of hydrogen in a range of 2 to 5 ppm.

According to claim 9, in addition to any of claims 1 to 8, the evaporation of the vapor-depositing material is carried out under a partial pressure of oxygen equal to or higher than 10^{-3} Pa.

According to claim 10, in addition to any of claims 1 to 9, the work is a rare earth metal-based permanent magnet.

According to claim 11, there is provided a surface treating apparatus comprising a vacuum treating chamber connected to a

evacuating system, a melting/evaporating source for melting and evaporating a wire-shaped vapor-depositing material containing a vapor deposition controlling gas, a member for retaining a work on which the vapor-depositing material is deposited, the melting/evaporating source and the work retaining member being disposed in the vacuum treating chamber, and a vapor-depositing material supply means for supplying the wire-shaped vapor-depositing material containing the vapor deposition controlling gas to the melting/evaporating source.

According to claim 12, in addition to claim 11, the vapor-depositing material supply means comprises a feed reel for feeding the wire-shaped vapor-depositing material.

According to claim 13, in addition to claim 11 or 12, the vapor deposition controlling gas is hydrogen gas.

According to claim 14, in addition to any of claims 11 to 13, the molar ratio of the vapor deposition controlling gas to oxygen can be adjusted by the feed rate of the vapor-depositing material fed from the feed reel.

[0006]

[MODE FOR CARRYING OUT THE INVENTION]

The type of the work to be subjected to the surface treatment in the surface treating process according to the present invention is particularly not limited, and may be any article if a vapor deposition treatment can be applied, such as a rare earth metal-based permanent magnet. However, the surface treating process according to the present invention is

particularly suitable for the surface treatment of an article that needs to be continuously treated in bulk, e.g., an electronic part material comprising a rare earth metal-based permanent magnet, because the time taken for an evacuation can be shortened in this surface treating process.

The surface treating process according to the present invention is also applicable to the formation of a film by merely heating and evaporating a vapor-depositing material, and to the formation of a film by ionizing the evaporated vapor-depositing material, for example, as in an ion plating process.

In addition, because the time taken for an evacuation can be shortened in this surface treating process, for example, to a range of 10 to 20 minutes, a productivity can be improved.

The structure of the surface treating apparatus for carrying out this surface treating process is very simple, because the volume of gas can be controlled by the feed rate of wire. In addition, hydrogen gas is produced from the wire in an apparatus which has relatively low degree of vacuum, therefore, oxidization of the vapor-depositing material can be prevented under a predetermined partial pressure of hydrogen.

[0007]

The type of the easily oxidizable vapor-depositing material used in the surface treating process according to the present invention is particularly not limited, and may be any material. For example, use of aluminum and the like, which is oxidized promptly even in the presence of a very small amount

of oxygen, is suitable for the vapor deposition treatment. Examples of the material other than aluminum are titanium, zinc, tin, lead, bismuth and the like.

[0008]

In the surface treating process according to the present invention, it is not necessary to make an entire atmosphere in a vacuum treating chamber to a vapor deposition controlling gas atmosphere, but it is necessary that a vapor deposition controlling gas atmosphere has been produced in at least zones near a vapor-depositing material and a work.

More particularly, when the control of the atmosphere is made by using hydrogen gas produced from the source of vapor deposition, it is preferable to produce the hydrogen gas resulting in the molar ratio of hydrogen to oxygen in at least the space between the vapor-depositing material and the work within the vacuum treating chamber in a range of 10 to 250, more preferably in a range of 20 to 150.

The reasons for the above are as follows. When the control of the atmosphere is made by using hydrogen gas produced from the source of vapor deposition, if the molar ratio is smaller than 10, an oxide film is formed on the surface of the molten vapor-depositing material within the melting/evaporating source to make the vapor deposition impossible, if the molar ratio exceeds 250, the boiling occurs on the surface of the molten vapor-depositing material within the melting/evaporating source and the degree of vacuum is reduced due to a rise in total

pressure in the treating chamber, whereby the vapor-depositing material is hard to evaporate, thus making the vapor deposition also impossible. Therefore, it is preferable to make the molar ratio of hydrogen to oxygen in a range of 20 to 150 as described above in order to ensure the vapor deposition.

[0009]

According to the reviews made by the present inventors, when the control of the atmosphere is made by using hydrogen gas produced from the source of vapor deposition, it is preferable to evaporate the vapor-depositing material resulting in a hydrogen concentration in the vapor deposited film in a range of 1 to 20 ppm, and more preferably to evaporate the vapor-depositing material resulting in a hydrogen concentration in the vapor deposited film in a range of 2 to 15 ppm.

[0010]

According to the present invention, when the control of the atmosphere is made by using hydrogen gas produced from the source of vapor deposition, in order to accurately control the molar ratio of hydrogen to oxygen or the hydrogen concentration in the vapor deposited film in a predetermined range, a wire-shaped vapor-depositing material containing hydrogen is evaporated while supplying such material to the melting/evaporating source of the vapor-depositing material.

With this wire-shaped vapor-depositing material, the molar ratio of hydrogen to oxygen or the hydrogen concentration in the vapor deposited film can be adjusted in a desired range

by regulating the content of hydrogen in the wire-shaped vapor-depositing material or regulating the feed rate of the wire-shaped vapor-depositing material to the melting/evaporating source of the vapor-depositing material.

[0011]

A surface treating apparatus for carrying out the above-described surface treating process will now be described with reference to the accompanying drawings.

Figs.1 and 2 show an embodiment of the surface treating apparatus according to the present invention. A plurality of hearths 2, each of which is a melting/evaporating source for evaporating aluminum 10 as a vapor-depositing material, are disposed on a hearth support base 4 risen on a support table 3 in a lower portion of a vacuum treating chamber 1 connected to an evacuating system which is not shown. Two cage-shaped work retaining members 5 each formed of a net-shaped material are disposed side-by-side for rotation about rotary shafts 6 in an upper portion of the vacuum treating chamber 1.

The apparatus is designed, so that rare earth metal-based magnets 30 as works are placed into each of the work retaining members 5, and the aluminum 10 is evaporated from the hearth 2 heated to a predetermined temperature by a heating means (not shown), while rotating the work retaining members 5, thereby forming a vapor deposited film of aluminum on the surface of each of the rare earth metal-based permanent magnets 30 in the work retaining members 5.

[0012]

The above-described arrangement is particularly not different from that of the conventional surface treating apparatus, but in the apparatus according to the present invention, an aluminum wire 11 containing hydrogen regulated to a predetermined concentration, which is a vapor-depositing material, is wound and retained around a feed reel 20 inside a lower portion of the support table 3. The proceeding end of the aluminum wire 11 can be guided into a thermal resistant protective tube 21 facing toward an inner surface of the hearth 2. The aluminum wire 11 can be fed at a predetermined feed rate into the hearth 2 by a pair of feeding gears 23 mounted into the notched window 22 which is provided in a portion of the protective tube 21.

[0013]

Thus, when the hearth 2 is heated to the predetermined temperature, and the aluminum wire 11 is fed from the feed reel 20 toward the hearth 2, a predetermined amount of hydrogen can be released from the aluminum wire 11 upon melting of the aluminum wire 11 fed into the hearth 2, whereby the vapor-depositing material can be evaporated in a state in which a hydrogen gas atmosphere has been produced in at least the zones near the aluminum wire 11 as the vapor-depositing material and the rare earth metal-based permanent magnet as the work within the vacuum treating chamber 1.

[0014]

In this case, the molar ratio of hydrogen to oxygen within the vacuum treating chamber can be adjusted to a desired value by regulating the amount of hydrogen contained in the aluminum wire or the feed rate of the aluminum wire fed.

[0015]

[EXAMPLES]

Particular examples will be described below.

A known cast ingot was pulverized and then subjected sequentially to a pressing, a sintering, a heat treatment and a surface working, thereby producing a magnet test piece having a size of 23 x 10 x 6 mm and a composition of 17Nd-1Pt-75Fe-7B.

Then, the magnet test piece was placed into a vacuum treating chamber having an internal volume of 2.2 m^3, and then, the vacuum treating chamber was evacuated, until the entire internal pressure in the vacuum treating chamber reached 1.0×10^{-1} Pa. A partial pressure of oxygen in the vacuum treating chamber at this time was measured by a quadru-pole mass spectrometer, and the number of molecules of oxygen present in the space between the vapor-depositing material and the work in the apparatus was calculated with a volume of the space between the vapor-depositing material and the work in the apparatus being defined to be 0.1 m^3 and with an average temperature of the space between the vapor depositing material and the work during the vapor deposition being defined to be 200°C. The partial pressure of oxygen and the number of molecules of oxygen present in the

space are shown in Table 1.

[0016]

Then, an Ar gas was introduced into the vacuum treating chamber, so that the total pressure was equal to 1.0 Pa, and the surface of the magnet was cleaned by the surface sputtering. Thereafter, the magnet was subjected to an ion plating by applying a voltage of 1.5 kV to heat, melt, evaporate and ionize the aluminum wire.

The aluminum wires having different hydrogen contents as shown in the columns of Examples 1 to 6 and Comparative examples 1 and 2 in Table 1 were used, and it was examined whether the vapor deposition was possible or impossible.

At this time, the aluminum wire was fed at a feed rate of 3 g/min into each of the six hearths in the vacuum treating chamber.

At this time, the wire was fed at a feed rate of 3 g/min into each of the six dissolution boats in the vacuum treating chamber.

Shown in Table 1 are the amount of hydrogen produced per minute calculated from the content of hydrogen in the aluminum wire, the partial pressure of hydrogen during the vapor deposition measured by a quadru-pole mass spectrometer, and the number of molecules of hydrogen and oxygen produced per minute in the space between the vapor-depositing material and the work.

Also shown in Table 1 are the measured value of the amount of hydrogen in the aluminum film formed in each of Examples 1

to 6, which was measured by a glow discharge spectrometry (GDS).

[0017]

Table 1

	1	2	3	4	5	6	7	8	9
Com. Example 1	0.2	6.0E-08	1.7E-02	2.80E-01	1.37	16.5	×	surface oxidized	-
Example 1	0.8	2.4E-07	1.8E-02	5.50E-01	1.64	30.6	○	surface partially oxidized	1.1
Example 2	2.7	8.1E-07	1.7E-02	1.30E+00	2.39	76.5	◎	good	2.9
Example 3	4.3	1.3E-06	1.9E-02	5.10E+00	6.20	268.4	◎	good	4.2
Example 4	10.2	3.1E-06	1.8E-02	9.00E+00	10.09	500.0	○	slightly boiled	9.1
Com. Example 2	19.6	5.9E-06	1.8E-02	1.52E+01	16.29	844.4	×	boiled	-

1 : Amount of hydrogen contained in aluminum wire (ppm)

2 : Amount of gas produced (mol/(cm2・min))

3 : Partial pressure of oxygen (Pa)

4 : Partial pressure of hydrogen (Pa)

5 : Total pressure (Pa)

6 : Hydrogen/oxygen

7 : Whether vapor deposition is possible or impossible

8 : Situation of molten aluminum

9 : Amount of hydrogen contained in film (ppm)

Com. = Comparative

[0018]

As shown in Table 1, in Examples 1 to 6, aluminum could be deposited on the magnet. Particularly, in Examples 2 to 4,

the good vapor deposition could be achieved. On the other hand, in Comparative Example 1, the amount of hydrogen produced relative to residual oxygen was not sufficient and hence, an oxide film was formed on the surface of the molten aluminum, thereby making the vapor deposition impossible. In Comparative Example 2, the boiling of the molten aluminum occurred, whereby the stable vapor deposition could not be achieved. Moreover, the deterioration of the magnetic characteristic due to the occlusion of hydrogen in the permanent magnet was observed.

[0019]

Then, the rare earth metal-based permanent magnet having the aluminum film formed under the conditions in Example 2 was subjected to a corrosion resistance test for 500 hours under high-temperature and high-humidity conditions of 80°C and 90 % RH. As a result, (BH)max before the test was 30.7 MGOe; (BH)max after the test was 29.9 MGOe; and the deterioration of the magnetic characteristic was equal to or lower than 5 %. The rusting of the magnet was not observed, and it was found that the magnet had an excellent corrosion resistance.

[0020]

[EFFECT OF THE INVENTION]

According to the present invention, as described above, by evaporating a wire-shaped vapor-depositing material containing a vapor deposition controlling gas such as hydrogen gas, while supplying such material to the melting/evaporating

source of the vapor-depositing material, the vapor-depositing material can be evaporated in a state in which a desired gas atmosphere has been produced in at least zones near the vapor-depositing material and the work within the vacuum treating chamber, thus, a vapor deposited film can be formed from the easily oxidizable vapor-depositing material on the surface of a desired work without use of a special apparatus for providing a high degree of vacuum.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[Fig.1] A diagrammatic front view of an embodiment of a surface treating apparatus according to the present invention

[Fig.2] A diagrammatic enlarged perspective view of an essential portion of the surface treating apparatus

[Fig.3] A diagrammatic front view of a conventional surface treating apparatus

[EXPLANATION OF REFERENCE CHARACTERS]

1 vacuum treating chamber

2 hearth

3 support table

4 hearth support base

5 work retaining member

6 rotary shaft

10 aluminum

11 aluminum wire

20 feed reel

21 protective tube

22 notched window

23 feeding gear

30 rare earth metal-based permanent magnet

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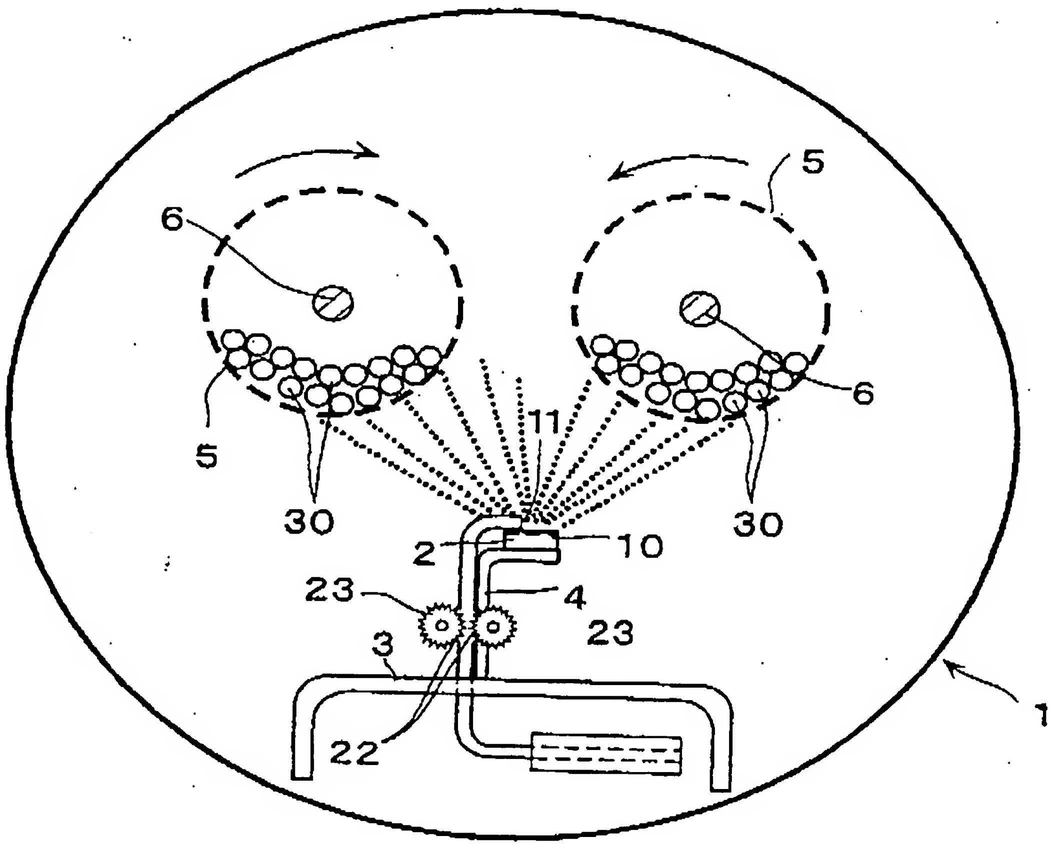
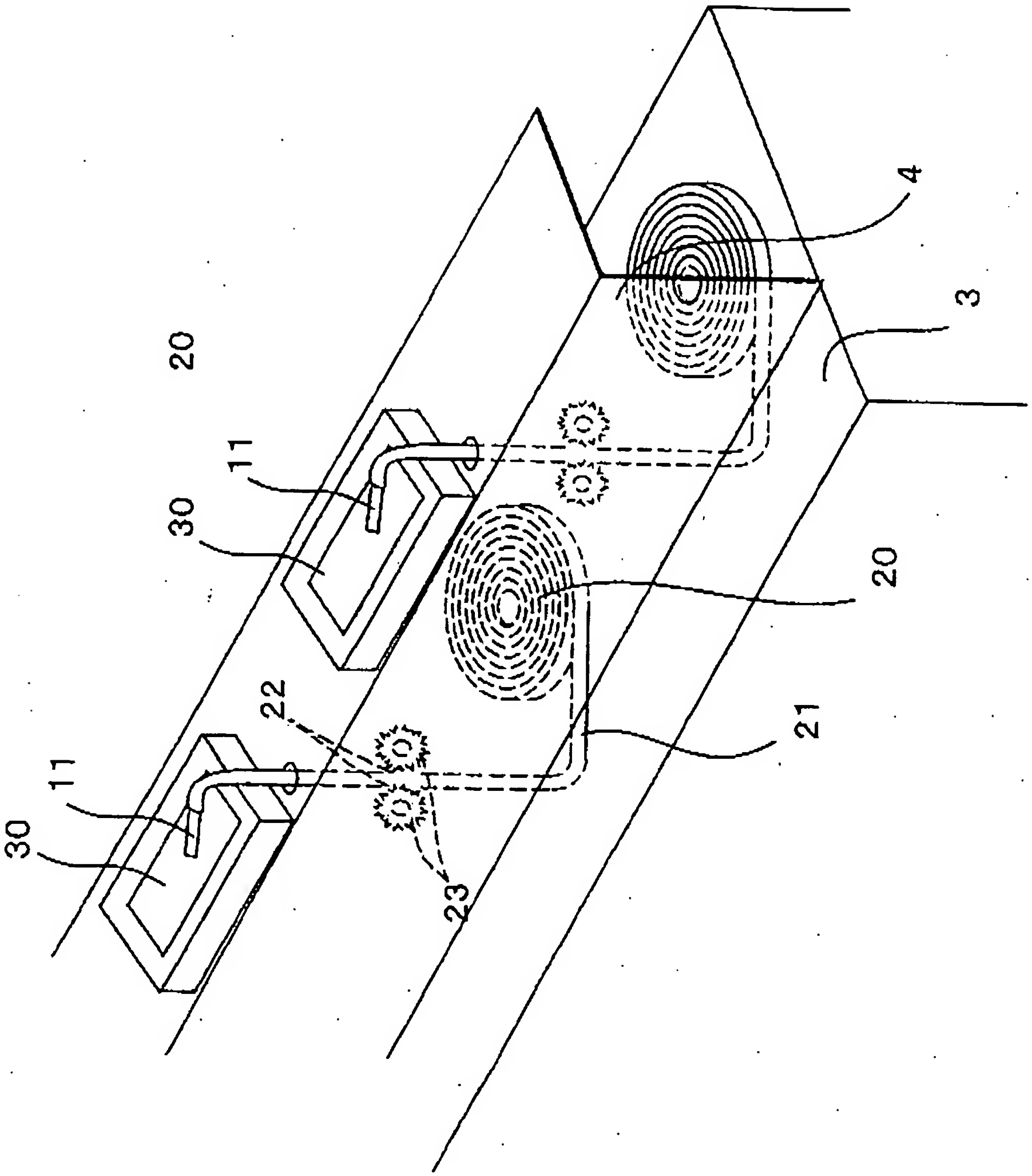
[NAME OF DOCUMENT] Drawings

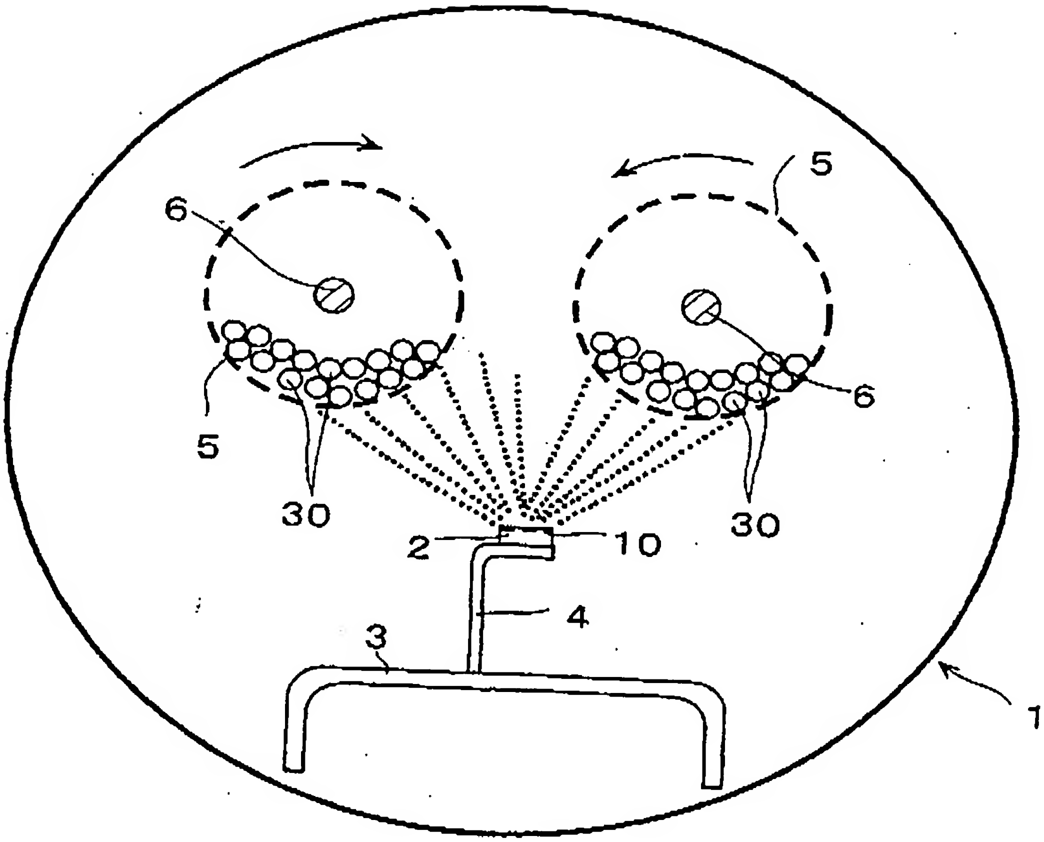
[FIG. 1]



[FIG. 2]



[FIG. 3]



[NAME OF DOCUMENT] ABSTRACT

[ABSTRACT]

[SUBJECT] It is an object of the present invention to provide a surface treating process for vapor-depositing an easily oxidizable material such as aluminum onto a work such as a rare earth metal-based permanent magnet, and a surface treating apparatus for carrying out the surface treating process.

[MEANS FOR SOLUTION] A surface treating process for forming a vapor deposited film from an easily oxidizable vapor-depositing material such as aluminum on the surface of a work such as a rare earth metal-based permanent magnet, in a state in which a desired vapor deposition controlling gas atmosphere has been produced in at least zones near the vapor-depositing material and the work, by evaporating a wire-shaped vapor-depositing material containing a vapor deposition controlling gas, while supplying such material to the melting/evaporating source of the vapor-depositing material; such surface treating process using a surface treating apparatus comprising a vacuum treating chamber connected to a evacuating system, a melting/evaporating source for melting and evaporating the vapor-depositing material, a member for retaining a work on which the vapor-depositing material is deposited, and a vapor-depositing material supply means for supplying the wire-shaped vapor-depositing material containing the vapor deposition controlling gas to the melting/evaporating source, the melting/evaporating source, the work retaining member, and the vapor-depositing material

supply means being disposed in the vacuum treating chamber.

[SELECTED DRAWING] Fig.1

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This is to certify that the annexed is a true copy of the following application as filed n this Office.

出 願 年 月 日 ate of Application:	１９９９年　５月１４日
願 番 号 plication Number:	平成１１年特許願第１３４９９９号
願 人 cant (s):	住友特殊金属株式会社

２０００年　５月１２日

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This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application: May 14, 1999

Application Number: Patent Application No. 11-134999

Applicant(s): Sumitomo Special Metals Co., Ltd.

May 12, 2000

Commissioner,
Patent Office Takahiko Kondo

Certificate No. 2000-3034444

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[NAME OF DOCUMENT] PATENT APPLICATION
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[TO] Commissioner, Patent Office
[INTERNATIONAL CLASSIFICATION] C23C 14/00
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[NAME OF DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION] SURFACE TREATING PROCESS AND RARE EARTH METAL-BASED PERMANENT MAGNET WITH SURFACE TREATED

[SCOPE OF CLAIMS OF PATENT]

[CLAIM 1] A surface treating process for forming a vapor deposited film from an easily oxidizable vapor-depositing material on the surface of a work, comprising the step of evaporating the vapor-depositing material in a state in which a vapor deposition controlling gas atmosphere has been produced in at least zones near a vapor-depositing material and the work.

[CLAIM 2] A surface treating process according to claim 1, wherein said vapor deposition controlling gas is hydrogen gas.

[CLAIM 3] A surface treating process according to claim 2, wherein the molar ratio of hydrogen to oxygen in at least a space between the vapor-depositing material and the work within the vacuum treating chamber is in a range of 10 to 250.

[CLAIM 4] A surface treating process according to claim 3, wherein the molar ratio of hydrogen to oxygen in at least a space between the vapor-depositing material and the work within the vacuum treating chamber is in a range of 20 to 150.

[CLAIM 5] A surface treating process according to claim 2, wherein said vapor-depositing material is evaporated resulting in a hydrogen concentration in said vapor deposited film in a range of 1 to 20 ppm.

[CLAIM 6] A surface treating process according to claim 5, wherein said vapor-depositing material is evaporated resulting

in a hydrogen concentration in said vapor deposited film in a range of 2 to 15 ppm.

[CLAIM 7] A surface treating process according to any of claims 1 to 6, wherein the evaporation of said vapor-depositing material is carried out under a partial pressure of oxygen equal to or higher than 10^{-3} Pa.

[CLAIM 8] A surface treating process according to any of claims 1 to 7, wherein said easily oxidizable vapor-depositing material is aluminum, titanium, zinc, tin, lead or bismuth.

[CLAIM 9] A surface treating process according to any of claims 1 to 8, wherein said work is a rare earth metal-based permanent magnet.

[CLAIM 10] A rare earth metal-based permanent magnet having a vapor deposited film formed thereon from aluminum, titanium, zinc, tin, lead or bismuth by a surface treating process according to any of claims 1 to 9.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[TECHNICAL FIELD TO WHICH THE INVENTION BELONGS]

The present invention relates to a surface treating process for vapor-depositing an easily oxidizable material such as aluminum and zinc onto a work such as a rare earth metal-based permanent magnet, and a rare earth metal-based permanent magnet produced by such process.

[0002]

[PRIOR ART]

For a rare earth metal-based permanent magnet having a nature that it is liable to be deteriorated by oxidation, for example, it is a conventional practice to form an aluminum film on the surface of the magnet by vapor deposition to prevent the deterioration of the magnet caused by oxidation. A surface treating apparatus, for example, as shown in Fig.3, is employed for such a treating process.

Fig.3 shows an apparatus for forming a vapor deposited film of aluminum on a magnet, more specifically, a rare earth metal-based permanent magnet. A plurality of hearths 2, each of which is a melting/evaporating source for evaporating aluminum 10 as a vapor-depositing material, are disposed on a hearth support base 4 risen on a support table 3 in a lower portion of a vacuum treating chamber 1 connected to an evacuating system which is not shown. Two cage-shaped work retaining members 5 each formed of a net-shaped material are disposed side-by-side for rotation about rotary shafts 6 in an upper portion of the vacuum treating chamber 1.

This apparatus is designed, so that rare earth metal-based magnets 30 as works are placed into each of the work retaining members 5, and the aluminum 10 is evaporated from the hearth 2 heated to a predetermined temperature by a heating means (not shown), while rotating the work retaining members 5, thereby forming a vapor deposited film of aluminum on the surface of each of the rare earth metal-based permanent magnets30 in the work retaining members 5.

[0003]

[PROBLEM TO BE SOLVED BY THE INVENTION]

However, when the vapor deposition process is carried out using such vapor deposition apparatus in an atmosphere particularly under a high partial pressure of oxygen in the vacuum treating chamber, the aluminum evaporated from the melting/evaporating source, before reaching the works, is oxidized and as a result, an aluminum film having an excellent quality cannot be formed. In addition, the apparatus suffers from a problem that an aluminum oxide film is formed on the molten aluminum within the melting/evaporating source and for this reason, aluminum as the evaporating material is sufficiently not evaporated. If an attempt is made to increase the degree of vacuum for reducing the partial pressure of oxygen, it is necessary to carry out an evacuation for a long time. Therefore, if the time taken for the overall processing is supposed to be, for example, 2.5 hours, one hour is required for providing a degree of vacuum equal to or lower than 10^{-4} Pa, resulting in a problem of a poor productivity.

[0004]

[MEANS FOR SOLUTION OF PROBLEM]

Accordingly, as a result of zealous studies made to solve the above problems, the present inventors have found that by evaporating the vapor-depositing material in a state in which a vapor deposition controlling gas atmosphere such as hydrogen gas has been produced in zones near the vapor-depositing material

and the work within the vacuum treating chamber, the problems which existed in a conventional process as described above can be solved without use of a special apparatus for providing a high degree of vacuum.

[0005]

A surface treating process according to the present invention has been accomplished based on the above knowledge in view, and to achieve the above object, according to claim 1, there is provided a surface treating process for forming a vapor deposited film from an easily oxidizable vapor-depositing material on the surface of a work, comprising the step of evaporating the vapor-depositing material in a state in which a vapor deposition controlling gas atmosphere has been produced in at least zones near a vapor-depositing material and the work.

According to claim 2, in addition to claim 1, the vapor deposition controlling gas is hydrogen gas.

According to claim 3, in addition to claim 2, the molar ratio of hydrogen to oxygen in at least a space between the vapor-depositing material and the work within the vacuum treating chamber is in a range of 10 to 250.

According to claim 4, in addition to claim 3, the molar ratio of hydrogen to oxygen in at least a space between the vapor-depositing material and the work within the vacuum treating chamber is in a range of 20 to 150.

According to claim 5, in addition to claim 2, the vapor-depositing material is evaporated resulting in a hydrogen

concentration in the vapor deposited film in a range of 1 to 20 ppm.

According to claim 6, in addition to claim 5, the vapor-depositing material is evaporated resulting in a hydrogen concentration in the vapor deposited film in a range of 2 to 15 ppm.

According to claim 7, in addition to any of claims 1 to 6, the evaporation of the vapor-depositing material is carried out under a partial pressure of oxygen equal to or higher than 10^{-3} Pa.

According to claim 8, in addition to any of claims 1 to 7, the easily oxidizable vapor-depositing material is aluminum, titanium, zinc, tin, lead or bismuth.

According to claim 9, in addition to any of claims 1 to 8, the work is a rare earth metal-based permanent magnet.

According to the present invention, there is provided a rare earth metal-based permanent magnet having a vapor deposited film formed thereon from aluminum, titanium, zinc, tin, lead or bismuth by a surface treating process according to any of claims 1 to 9.

[0006]

[MODE FOR CARRYING OUT THE INVENTION]

The type of the work to be subjected to the surface treatment in the surface treating process according to the present invention is particularly not limited, and may be any article if a vapor deposition treatment can be applied, such as a rare

earth metal-based permanent magnet. However, the surface treating process according to the present invention is particularly suitable for the surface treatment of an article that needs to be continuously treated in bulk, e.g., an electronic part material comprising a rare earth metal-based permanent magnet, because the time taken for an evacuation can be shortened in this surface treating process.

The surface treating process according to the present invention is also applicable to the formation of a film by merely heating and evaporating a vapor-depositing material, and to the formation of a film by ionizing the evaporated vapor-depositing material, for example, as in an ion plating process.

In addition, because the time taken for an evacuation can be shortened in this surface treating process, for example, to a range of 10 to 20 minutes, a productivity can be improved.

[0007]

The type of the easily oxidizable vapor-depositing material used in the surface treating process according to the present invention is particularly not limited, and may be any material. For example, use of aluminum and the like, which is oxidized promptly even in the presence of a very small amount of oxygen, is suitable for the vapor deposition treatment. Examples of the material other than aluminum are titanium, zinc, tin, lead, bismuth and the like.

[0008]

In the surface treating process according to the present

invention, it is not necessary to make an entire atmosphere in a vacuum treating chamber to a vapor deposition controlling gas atmosphere, but it is necessary that a vapor deposition controlling gas atmosphere has been produced in at least zones near a vapor-depositing material and a work.

More particularly, when the control of the atmosphere is made by using hydrogen gas produced from the source of vapor deposition, it is preferable to produce the hydrogen gas resulting in the molar ratio of hydrogen to oxygen in at least the space between the vapor-depositing material and the work within the vacuum treating chamber in a range of 10 to 250, more preferably in a range of 20 to 150.

The reasons for the above are as follows. When the control of the atmosphere is made by using hydrogen gas produced from the source of vapor deposition, if the molar ratio is smaller than 10, an oxide film is formed on the surface of the molten vapor-depositing material within the melting/evaporating source to make the vapor deposition impossible, if the molar ratio exceeds 250, the boiling occurs on the surface of the molten vapor-depositing material within the melting/evaporating source and the degree of vacuum is reduced due to a rise in total pressure in the treating chamber, whereby the vapor-depositing material is hard to evaporate, thus making the vapor deposition also impossible. Therefore, it is preferable to make the molar ratio of hydrogen to oxygen in a range of 20 to 150 as described above in order to ensure the vapor deposition.

[0009]

According to the reviews made by the present inventors, when the control of the atmosphere is made by using hydrogen gas produced from the source of vapor deposition, it is preferable to evaporate the vapor-depositing material resulting in a hydrogen concentration in the vapor deposited film in a range of 1 to 20 ppm, and more preferably to evaporate the vapor-depositing material resulting in a hydrogen concentration in the vapor deposited film in a range of 2 to 15 ppm.

[0010]

If a rare earth metal-based permanent magnet such as an R-Fe-B based permanent magnet is selected as the work, and a vapor deposited film of aluminum is formed on the rare earth metal-based permanent magnet, the rare earth metal-based permanent magnet can be coated in an adhered manner with the aluminum film having an excellent quality. Therefore, it is possible to easily and reliably produce a rare earth metal-based permanent magnet having an excellent corrosion resistance. The rare earth metal-based permanent magnet produced by the process according to the present invention and having a film of aluminum, may be subjected to a known treatment such as a chromate treatment, a shot peening and the like for the purpose of further enhancing the corrosion resistance.

[0011]

A surface treating apparatus for carrying out the above-described surface treating process will now be described

with reference to the accompanying drawings.

Figs.1 and 2 show an embodiment of the surface treating apparatus according to the present invention. A plurality of hearths 2, each of which is a melting/evaporating source for evaporating aluminum 10 as a vapor-depositing material, are disposed on a hearth support base 4 risen on a support table 3 in a lower portion of a vacuum treating chamber 1 connected to an evacuating system which is not shown. Two cage-shaped work retaining members 5 each formed of a net-shaped material are disposed side-by-side for rotation about rotary shafts 6 in an upper portion of the vacuum treating chamber 1.

The apparatus is designed, so that rare earth metal-based magnets 30 as works are placed into each of the work retaining members 5, and the aluminum 10 is evaporated from the hearth 2 heated to a predetermined temperature by a heating means (not shown), while rotating the work retaining members 5, thereby forming a vapor deposited film of aluminum on the surface of each of the rare earth metal-based permanent magnets 30 in the work retaining members 5.

[0012]

The above-described arrangement is particularly not different from that of the conventional surface treating apparatus, but in the apparatus according to the present invention, an aluminum wire 11 containing hydrogen regulated to a predetermined concentration, which is a vapor-depositing material, is wound and retained around a feed reel 20 inside

a lower portion of the support table 3. The proceeding end of the aluminum wire 11 can be guided into a thermal resistant protective tube 21 facing toward an inner surface of the hearth 2. The aluminum wire 11 can be fed at a predetermined feed rate into the hearth 2 by a pair of feeding gears 23 mounted into the notched window 22 which is provided in a portion of the protective tube 21.

[0013]

Thus, when the hearth 2 is heated to the predetermined temperature, and the aluminum wire 11 is fed from the feed reel 20 toward the hearth 2, a predetermined amount of hydrogen can be released from the aluminum wire 11 upon melting of the aluminum wire 11 fed into the hearth 2, whereby the vapor-depositing material can be evaporated in a state in which a hydrogen gas atmosphere has been produced in at least the zones near the aluminum wire 11 as the vapor-depositing material and the rare earth metal-based permanent magnet as the work within the vacuum treating chamber 1.

[0014]

In this case, the molar ratio of hydrogen to oxygen within the vacuum treating chamber can be adjusted to a desired value by regulating the amount of hydrogen contained in the aluminum wire or the feed rate of the aluminum wire fed.

The method for producing a hydrogen gas atmosphere in zones near the vapor-depositing material and the work within the vacuum treating chamber 1 is not limited to the above mentioned method

using the aluminum wire, wherein for example, hydrogen gas is introduced to zones near the source of vapor deposition by a pipe.

For supplying hydrogen gas, 2 or more methods may be adopted in combination.

[0015]

[EXAMPLES]

Particular examples will be described below.

A known cast ingot was pulverized and then subjected sequentially to a pressing, a sintering, a heat treatment and a surface working, thereby producing a magnet test piece having a size of 23 x 10 x 6 mm and a composition of 17Nd-1Pt-75Fe-7B.

Then, the magnet test piece was placed into a vacuum treating chamber having an internal volume of 2.2 m^3, and then, the vacuum treating chamber was evacuated, until the entire internal pressure in the vacuum treating chamber reached 1.0 x 10^{-1} Pa. A partial pressure of oxygen in the vacuum treating chamber at this time was measured by a quadru-pole mass spectrometer, and the number of molecules of oxygen present in the space between the vapor-depositing material and the work in the apparatus was calculated with a volume of the space between the source of vapor deposition and the work in the apparatus being defined to be 0.1 m^3 and with an average temperature of the space between the vapor depositing material and the work during the vapor deposition being defined to be 200°C. The

partial pressure of oxygen and the number of molecules of oxygen present in the space are shown in Table 1.

[0016]

Then, an Ar gas was introduced into the vacuum treating chamber, so that the total pressure was equal to 1.0 Pa, and the surface of the magnet was cleaned by the surface sputtering. Thereafter, the magnet was subjected to an ion plating by applying a voltage of 1.5 kV to heat, melt, evaporate and ionize the aluminum wire.

The aluminum wires having different hydrogen contents as shown in the columns of Examples 1 to 6 and Comparative examples 1 and 2 in Table 1 were used, and it was examined whether the vapor deposition was possible or impossible.

At this time, the aluminum wire was fed at a feed rate of 3 g/min into each of the six hearths in the vacuum treating chamber.

Shown in Table 1 are the amount of hydrogen produced per minute calculated from the content of hydrogen in the aluminum wire, the partial pressure of hydrogen during the vapor deposition measured by a quadru-pole mass spectrometer, and the number of molecules of hydrogen and oxygen produced per minute in the space between the vapor-depositing material and the work.

Also shown in Table 1 are the measured value of the amount of hydrogen in the aluminum film formed in each of Examples 1 to 6, which was measured by a glow discharge spectrometry (GDS).

[0017]

Table 1

	1	2	3	4	5	6	7	8	9
Com. Example 1	0.2	6.0E-08	1.7E-02	2.80E-01	1.37	16.5	×	surface oxidized	-
Example 1	0.8	2.4E-07	1.8E-02	5.50E-01	1.64	30.6	○	surface partially oxidized	1.1
Example 2	2.7	8.1E-07	1.7E-02	1.30E+00	2.39	76.5	◎	good	2.9
Example 3	4.3	1.3E-06	1.9E-02	5.10E+00	6.20	268.4	◎	good	4.2
Example 4	10.2	3.1E-06	1.8E-02	9.00E+00	10.09	500.0	○	slightly boiled	9.1
Com. Example 2	19.6	5.9E-06	1.8E-02	1.52E+01	16.29	844.4	×	boiled	-

1 : Amount of hydrogen contained in aluminum wire (ppm)

2 : Amount of gas produced (mol/(cm2・min))

3 : Partial pressure of oxygen (Pa)

4 : Partial pressure of hydrogen (Pa)

5 : Total pressure (Pa)

6 : Hydrogen/oxygen

7 : Whether vapor deposition is possible or impossible

8 : Situation of molten aluminum

9 : Amount of hydrogen contained in film (ppm)

Com. = Comparative

[0018]

As shown in Table 1, in Examples 1 to 6, aluminum could be deposited on the magnet. Particularly, in Examples 2 to 4, the good vapor deposition could be achieved. On the other hand, in Comparative Example 1, the amount of hydrogen produced

relative to residual oxygen was not sufficient and hence, an oxide film was formed on the surface of the molten aluminum, thereby making the vapor deposition impossible. In Comparative Example 2, the boiling of the molten aluminum occurred, whereby the stable vapor deposition could not be achieved. Moreover, the deterioration of the magnetic characteristic due to the occlusion of hydrogen in the permanent magnet was observed.

[0019]

Then, the rare earth metal-based permanent magnet having the aluminum film formed under the conditions in Example 2 was subjected to a corrosion resistance test for 500 hours under high-temperature and high-humidity conditions of 80°C and 90 % RH. As a result, (BH)max before the test was 30.7 MGOe; (BH)max after the test was 29.9 MGOe; and the deterioration of the magnetic characteristic was equal to or lower than 5 %. The rusting of the magnet was not observed, and it was found that the magnet had an excellent corrosion resistance.

[0020]

[EFFECT OF THE INVENTION]

According to the present invention, as described above, by evaporating the vapor-depositing material in a state in which a vapor deposition controlling gas atmosphere such as hydrogen gas has been produced in at least zones near the vapor-depositing material and the work within the vacuum treating chamber, the vapor deposited film can be formed from the easily oxidizable

vapor-depositing material on the surface of a desired work without use of a special apparatus for providing a high degree of vacuum. By employment of such a surface treating process, it is possible to provide a rare earth metal-based permanent magnet extremely liable to be oxidized, without degradation of a high magnetic characteristic of the magnet.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[Fig.1] A diagrammatic front view of an embodiment of a vacuum treating apparatus for carrying out a surface treating process according to the present invention

[Fig.2] A diagrammatic enlarged perspective view of an essential portion of the vacuum treating apparatus

[Fig.3] A diagrammatic front view of a vacuum treating apparatus for carrying out a conventional surface treating process

[EXPLANATION OF REFERENCE CHARACTERS]

1 vacuum treating chamber

2 hearth

3 support table

4 hearth support base

5 work retaining member

6 rotary shaft

10 aluminum

11 aluminum wire

20 feed reel

21 protective tube

22 notched window

23 feeding gear

30 rare earth metal-based permanent magnet

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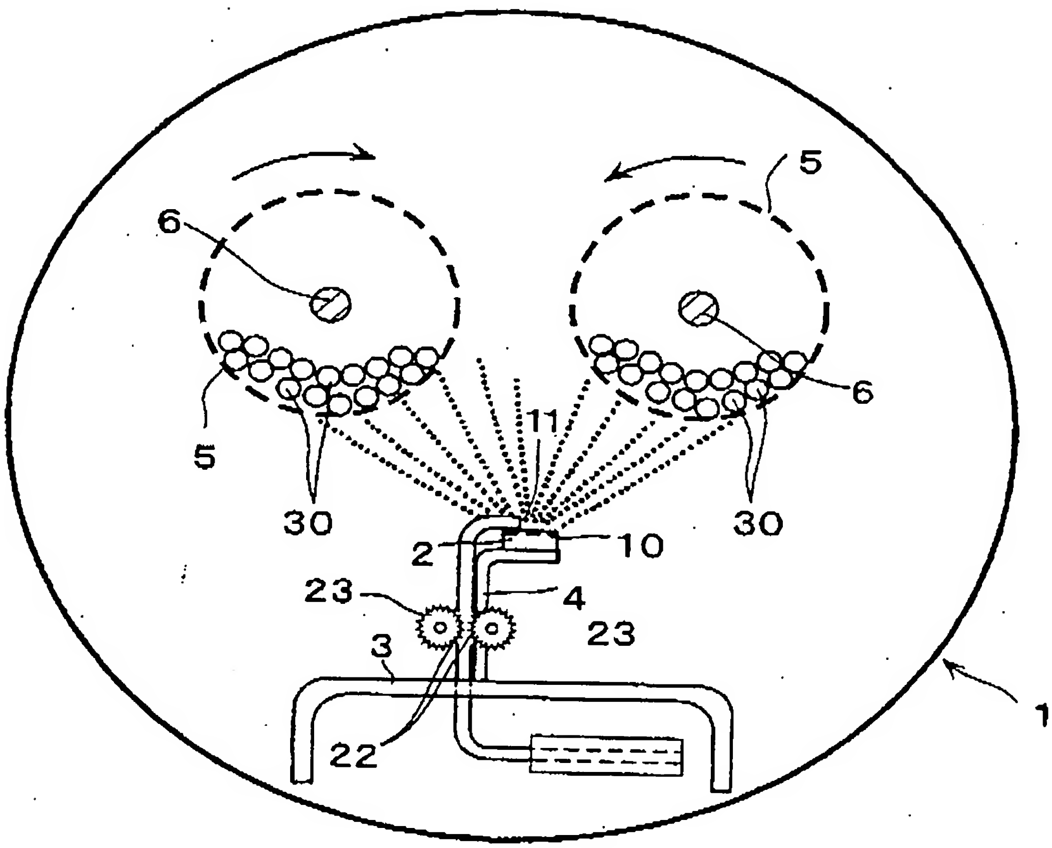
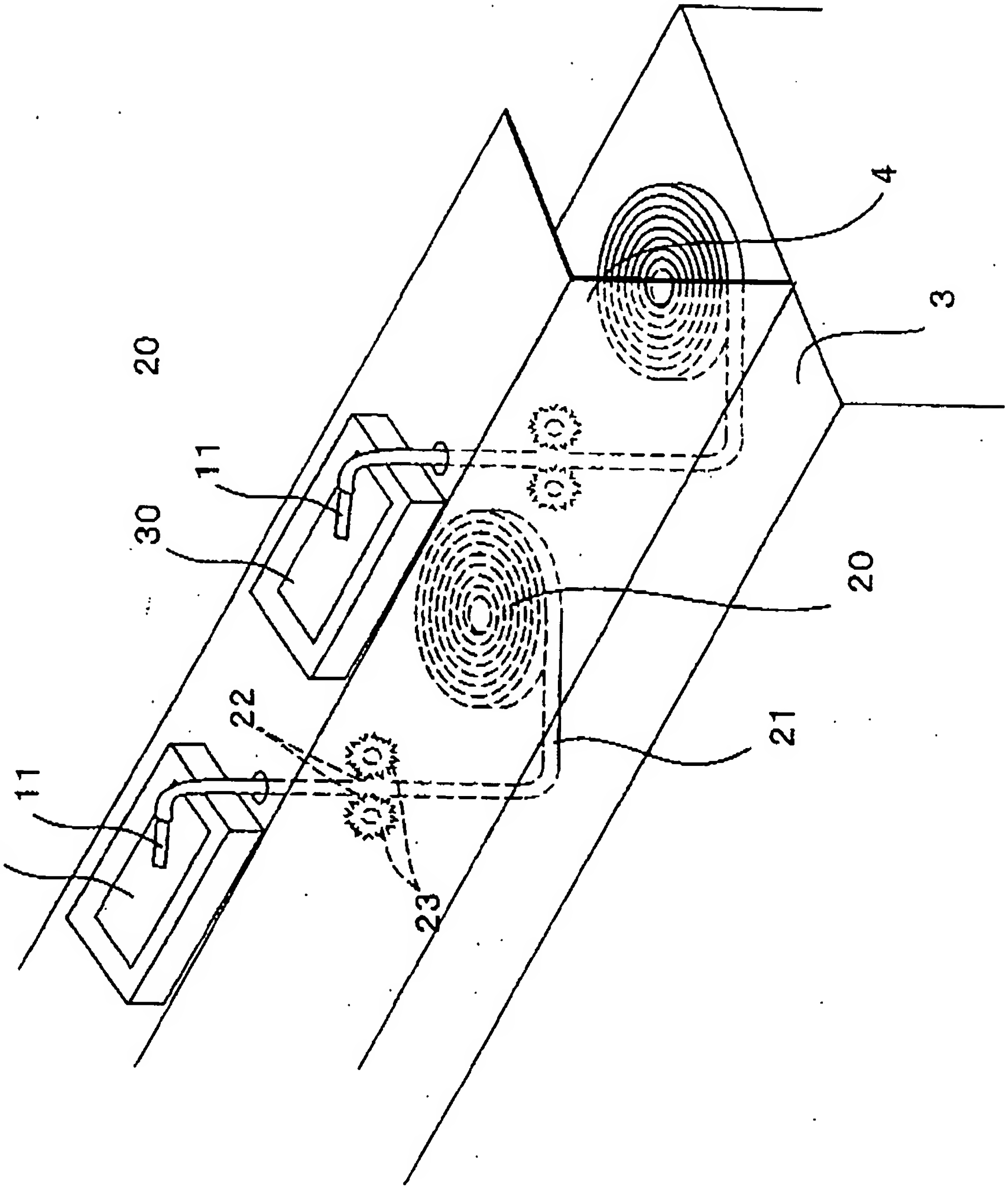
[NAME OF DOCUMENT] Drawings

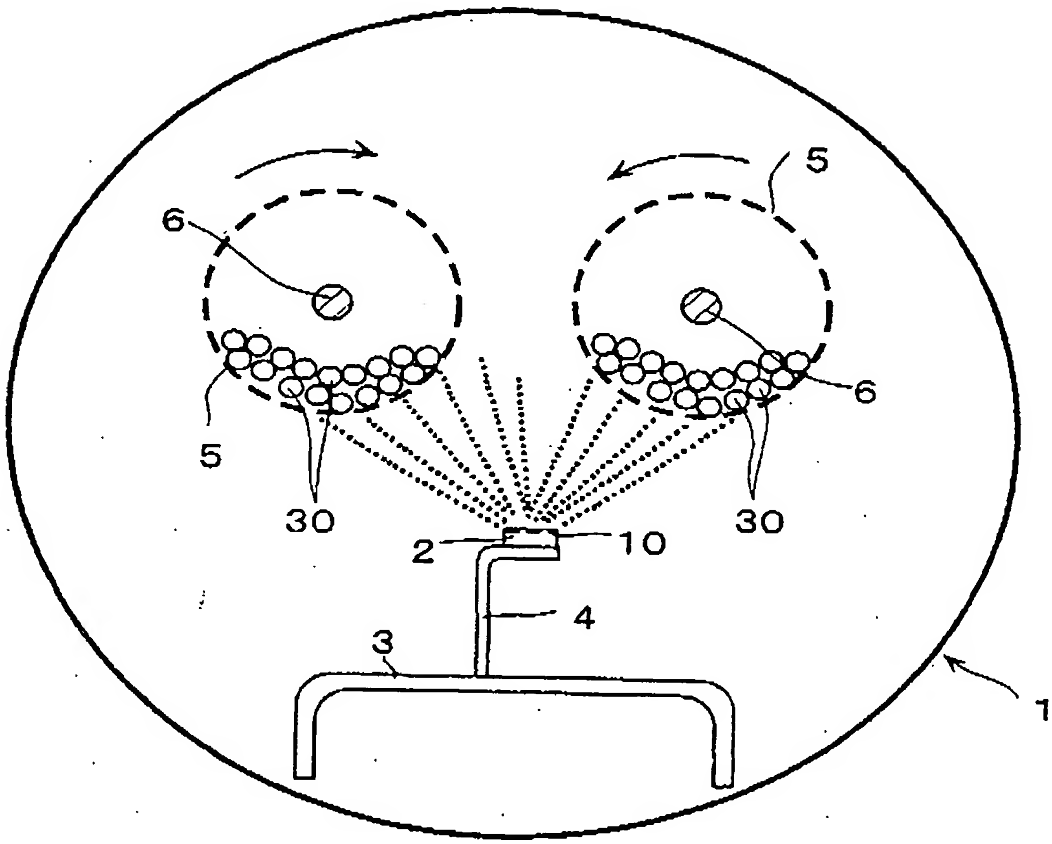
[FIG. 1]



[FIG. 2]



[FIG. 3]



[NAME OF DOCUMENT] ABSTRACT

[ABSTRACT]

[SUBJECT] It is an object of the present invention to provide a surface treating process for vapor-depositing an easily oxidizable material such as aluminum onto a work such as a rare earth metal-based permanent magnet.

[MEANS FOR SOLUTION] A surface treating process for forming a vapor deposited film from an easily oxidizable vapor-depositing material such as aluminum on the surface of a work such as a rare earth metal-based permanent magnet, comprising the step of evaporating the vapor-depositing material in a state in which a vapor deposition controlling gas atmosphere has been produced in at least zones near the vapor-depositing material and the work.

[SELECTED DRAWING] Fig.1